

Keywords: crystal structure; D-lyxose bisulfite adduct; potassium hydrogen sulfite; potassium metabisulfite; hydrogen bonding

CCDC reference: 1415264

Supporting information: this article has supporting information at journals.iucr.org/e

Crystal structure of potassium (1*S*)-D-lyxit-1-yl-sulfonate monohydrate

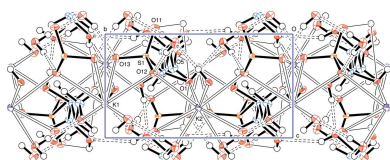
Alan H. Haines* and David L. Hughes*

School of Chemistry, University of East Anglia, Norwich NR4 7TJ, United Kingdom. *Correspondence e-mail: a.haines@uea.ac.uk, d.l.hughes@uea.ac.uk

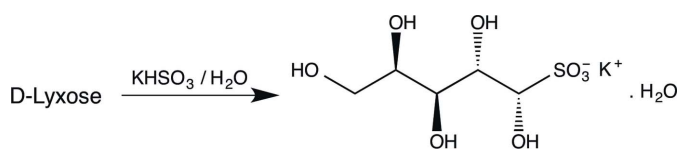
The title compound, $K^+ \cdot C_5H_{11}O_8S^- \cdot H_2O$ [systematic name: potassium (1*S*,2*S*,3*S*,4*R*)-1,2,3,4,5-pentahydropentane-1-sulfonate monohydrate], formed by reaction of D-lyxose with potassium hydrogen sulfite in water, crystallizes as colourless square prisms. The anion has an open-chain structure in which the S atom, the C atoms of the sugar chain and the oxygen atom of the hydroxymethyl group form an essentially all-*trans* chain with the corresponding torsion angles lying between 178.61 (12) and 157.75 (10)°. A three-dimensional bonding network exists in the crystal structure involving coordination of two crystallographically independent potassium ions by O atoms (one cation being hexa- and the other octa-coordinate, with each lying on a twofold rotation axis), and extensive intermolecular O—H...O hydrogen bonding.

1. Chemical context

In aqueous solution, the bisulfite anion HSO_3^- exists in a complex, pH-dependent equilibrium with sulfurous acid H_2SO_3 and the sulfite anion SO_3^{2-} . These sulfur compounds are widely used in the preservation of foodstuffs because of their anti-oxidant and antimicrobial properties. Dissolution of sodium or potassium metabisulfite ($Na_2S_2O_5$ or $K_2S_2O_5$, respectively) in water affords a mixture of such compounds, along with sulfur dioxide, and they are widely used (*e.g.* as food additive E223) for their anti-oxidant, bactericidal and preservative properties. The reaction of the bisulfite ion with carbonyl compounds to give hydroxysulfonic acids has long been known as a method of aldehyde purification; less well recognized generally is that reaction of an aldehyde-sugar, which exists predominantly in a cyclic, hemi-acetal form, with a bisulfite anion affords the open-chain form of the carbohydrate in which the carbonyl group has undergone addition of the sulfur nucleophile. A possible role in the stabilization of food stuffs led to early studies (Gehman & Osman, 1954) and evidence for the acyclic nature of such compounds was first provided by Ingles (1959), who reported on such adducts from D-glucose, D-galactose, D-mannose, L-arabinose and L-rhamnose. However, conclusive proof of the acyclic nature of these bisulfite adducts was first given through the X-ray studies of Cole *et al.* (2001) who reported the crystal structures of D-glucose- and D-mannose-derived potassium sulfonates. Later studies by X-ray crystallography on the sodium sulfonate derived from D-glucose (Haines & Hughes, 2012) and the potassium sulfonates from D-galactose (Haines & Hughes, 2010) and D-ribose (Haines & Hughes, 2014) proved their acyclic nature and allowed, in each case, the configuration at the newly formed chiral centre to be determined.



The crystallization of the bisulfite adducts of aldoses requires reactions to be conducted in concentrated solution, and success can be dependent on the particular aldose and the choice of the alkali metal ion. Thus, we have prepared the potassium adduct from L-arabinose as described by Ingles (1959), having properties in agreement with those reported, but despite prolonged efforts have not succeeded in obtaining suitable crystals for X-ray determination. Our attempts to make a crystalline potassium sulfonate from D-xylose have not been successful. In contrast, D-ribose readily afforded suitable crystals (Haines & Hughes, 2014) and we were therefore prompted to investigate the reaction of the remaining pentose, D-lyxose, with the bisulfite ion, from which we isolated the nicely crystalline title product (see Scheme). We report here its crystal structure.



2. Structural commentary

The systematic name for the salt is potassium (1*S*,2*S*,3*S*,4*R*)-1,2,3,4,5-pentahydroxypentane-1-sulfonate monohydrate. The anion has an open-chain structure in which the S atom, the C atoms of the sugar chain and the O atom of the hydroxymethyl group form an essentially all-*trans* chain with the corre-

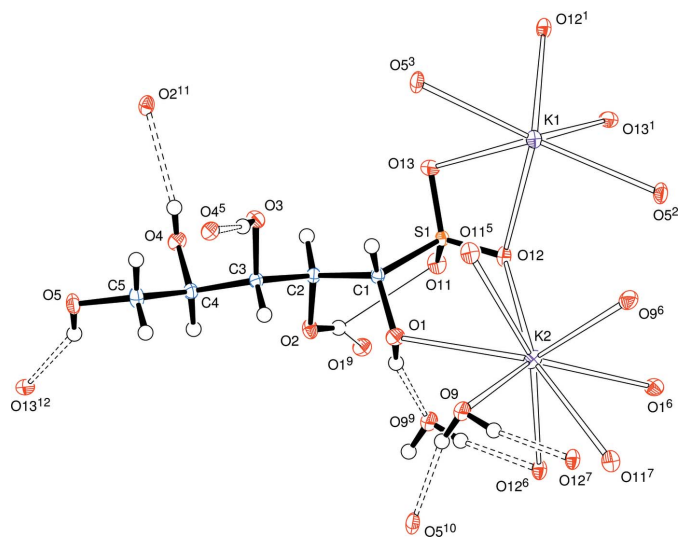


Figure 1
View of a molecule of a D-lyxose-KHSO₃ adduct and water molecule, indicating the atom-numbering scheme. The coordination spheres of the two potassium ions (both lying on twofold rotation axes), and the hydrogen bonds (dashed lines) on the lyxose unit, are shown. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (1) $-x + 1, -y + 2, z$; (2) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (3) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (4) $-x + 1, -y + 2, z + 1$; (5) $x, y, z + 1$; (6) $-x + 1, -y + 1, z$; (7) $-x + 1, -y + 1, z + 1$; (8) $x, y - 1, z$; (9) $x, y, z - 1$; (10) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (11) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (12) $-x + \frac{1}{2}, y - \frac{1}{2}, -z$.]

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1O···O9 ⁱ	0.80 (3)	1.90 (3)	2.6716 (19)	160 (2)
O2—H2O···O1 ⁱ	0.77 (3)	2.35 (3)	2.9810 (17)	141 (2)
O2—H2O···O11	0.77 (3)	2.41 (2)	2.9935 (16)	134 (2)
O3—H3O···O4 ⁱⁱ	0.85 (3)	1.91 (3)	2.7609 (17)	173 (3)
O4—H4O···O2 ⁱⁱⁱ	0.76 (3)	2.17 (3)	2.8586 (17)	151 (3)
O5—H5O···O13 ^{iv}	0.78 (3)	2.03 (3)	2.7152 (17)	146 (2)
O9—H9A···O5 ^v	0.81 (3)	1.95 (3)	2.7426 (18)	167 (3)
O9—H9B···O12 ^{vi}	0.84 (3)	1.90 (3)	2.7289 (17)	170 (3)

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y, z + 1$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (vi) $-x + 1, -y + 1, z + 1$.

sponding torsion angles lying between absolute values of 178.61 (12) (for C2—C3—C4—C5) and 157.75 (10)° (for S1—C1—C2—C3). The newly formed chiral centre at C1 has the *S* configuration (Fig. 1). For each lyxose residue, all hydroxy groups act as hydrogen-bond donors (Table 1). Atom H2O is involved in a bifurcated hydrogen bond to O11 in the same molecule and to O1 in a neighbouring molecule (at $x, y, z - 1$). Atom H1O is involved in hydrogen bonding to atom O9 of a water molecule, the H atoms of which are hydrogen-bonded to O5 and O12 of adjoining molecules. Two crystallographically independent potassium ions are present, each one lying on a twofold rotation axis, with one cation possessing a coordination sphere of six O atoms (assuming a cut-off distance of 3 Å), four coming from two different sulfonate residues and two from O atoms of hydroxymethyl groups. The other cation is octacoordinate with oxygen atoms arising from two water molecules, two O atoms at new chiral centres at C1, and from two pairs of O atoms from different sulfonate residues. The

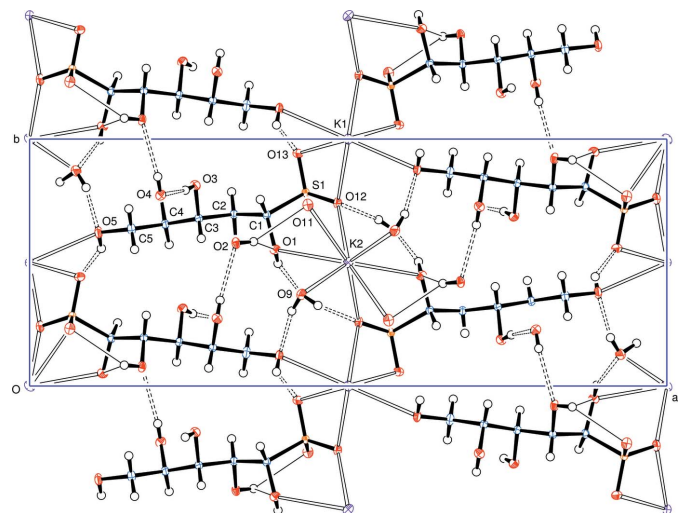


Figure 2
Packing diagram, viewed along the *c* axis, showing the approximately parallel alignment of the D-lyxose chains between sheets of potassium ions and water molecules. Hydrogen bonds are shown as dashed lines; the fine line bonds are of bifurcated hydrogen bonds. Please note that the atoms labelled O2, O4 and O11 are eclipsing the real atoms of those names.

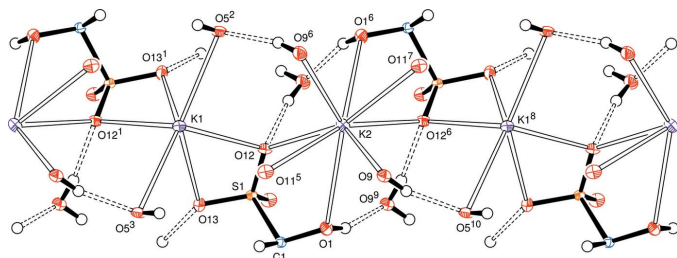


Figure 3

View (slightly offset from along the *c* axis) of the sheets of potassium ions which are linked through coordinating *D*-lyxose-sulfite anions and water molecules. Symmetry codes are as in Fig. 1.

range of cation–oxygen bond lengths in the coordination spheres lie in the range 2.7787 (12) to 2.9855 (12) Å, but it should be noted that the designated hexacoordinate potassium ion does have two further neighbouring O atoms at 3.1131 (12) and 3.3824 (13) Å. Variability in the coordination spheres of potassium ions in related coordination environments was observed in the *D*-galactose bisulfite (Haines & Hughes, 2010), *D*-glucose bisulfite (Cole *et al.* 2001; Haines & Hughes, 2012) and dehydro-*L*-ascorbic acid bisulfite (Haines & Hughes, 2013) adducts, where the potassium ion is, respectively, six-, seven- and eight-coordinate.

A view along the *c* axis (Fig. 2) indicates the approximately parallel but alternating alignment of the *D*-lyxose chains between sheets of potassium ions and water molecules, with hydrogen bonds shown as dashed bonds except for the bifurcated hydrogen bonds which are denoted by fine line bonds. Cation coordination with *D*-lyxose sulfite anions and water molecules is depicted in Fig. 3 and a view along the *a* axis (Fig. 4) shows the approximately parallel alignment of the *D*-lyxose chains.

3. Supramolecular features

A three-dimensional network exists in the crystal structure through coordination of (i) a hexacoordinate potassium ion with O atoms from four different *D*-lyxose bisulfite residues,

(ii) an octacoordinate potassium ion with O atoms from four different *D*-lyxose bisulfite residues and two different water molecules, (iii) intermolecular hydrogen bonding between hydroxy groups of the *D*-lyxose moieties, and (iv) hydrogen bonding between a water molecule and two different lyxose residues. Despite spectroscopic evidence for a diastereoisomeric adduct in solution, only the 1*S* stereoisomer crystallized from the reaction mixture.

4. Spectroscopic findings

High-resolution mass spectrometry in negative-ion mode showed no significant peak for $[(C_5H_{11}O_8S_1)^-]$ at the calculated *m/z* of 231.0180, but a significant peak was observed at 213.0073 $[(C_5H_{11}O_8S - H_2O)^-]$. A similar loss of water from the parent anion was observed in the case of the *D*-ribose adduct (Haines & Hughes, 2014). A peak at 149.0457 $[(C_5H_9O_5)^-]$ arose from the parent sugar and the base peak was at 299.0979 $[(C_{10}H_{19}O_{10})^-]$. The latter corresponds to the ion of the product formed by reaction between the bisulfite adduct and *D*-lyxose with displacement of potassium bisulfite.

The 1H NMR spectrum of the adduct in D_2O showed the presence the α - and β -pyranose forms of *D*-lyxose and the major and minor forms of the acyclic sulfonate in the % ratios of 35.48 : 11.29 : 48.39 : 4.84. The adduct undergoes partial hydrolysis in aqueous media; notably, it is present in a larger proportion in the more concentrated solution used for ^{13}C NMR spectroscopy (see below). A large $J_{2,3}$ coupling of 9.4 Hz suggests the conformation about the C2–C3 bond is similar in solution and the crystalline state.

In the ^{13}C NMR spectrum, signals for C1 nuclei allow identification of the α - and β -pyranose forms of *D*-lyxose and the major (δ_C 82.20) and minor (δ_C 84.26) adducts in the ratios of 17.05 : 5.43 : 71.32 : 6.20, respectively.

5. Synthesis and crystallization

Water (0.5 ml) was added to potassium metabisulfite (0.37 g) which did not completely dissolve even on warming but which

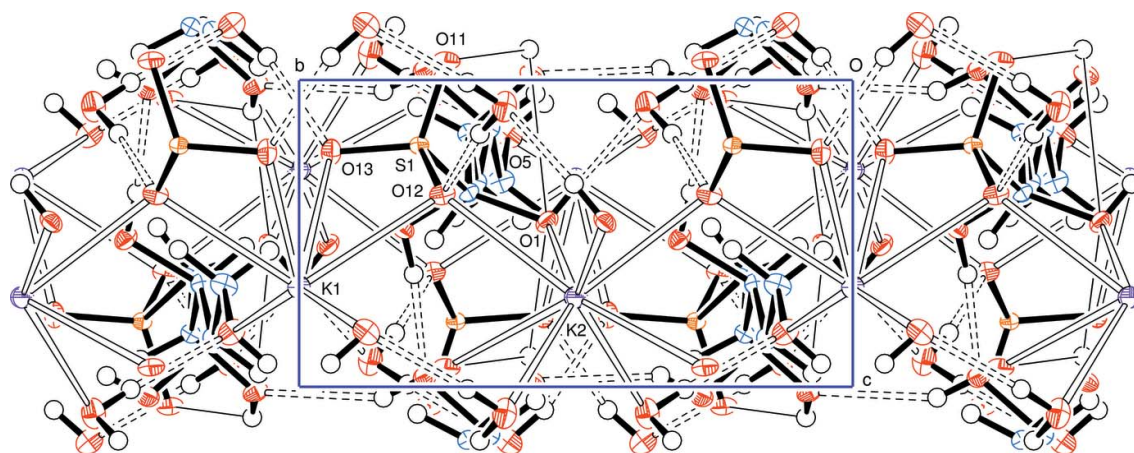


Figure 4

View along the *a* axis, showing the approximately parallel alignment of the *D*-lyxose chains.

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{K}^+\cdot\text{C}_5\text{H}_{11}\text{O}_8\text{S}^-\cdot\text{H}_2\text{O}$
M_r	288.31
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	140
a, b, c (Å)	23.3536 (5), 9.0434 (2), 4.9939 (1)
V (Å ³)	1054.69 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.74
Crystal size (mm)	0.28 × 0.26 × 0.11
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3/ Sapphire3 CCD
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2014)
$T_{\text{min}}, T_{\text{max}}$	0.914, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20712, 3062, 3008
R_{int}	0.023
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.018, 0.048, 1.12
No. of reflections	3062
No. of parameters	198
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.30, -0.34
Absolute structure	Flack x determined using 1229 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.023 (11)

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) *ORTEP* (Johnson, 1976), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

appeared to change its crystalline form as it underwent hydrolysis to yield potassium hydrogen sulfite. To this suspension was added a solution of D-lyxose (0.5 g) in water (0.35 ml), leading to immediate and complete solution of the reaction mixture. Seed crystals were obtained by evaporation of a small proportion of the solution, and these were added to the bulk of the solution which was then stored at 277 K, leading to the formation of large, well separated crystals. The mother liquor was removed with a Pasteur pipette, and the crystals were dried by pressing between filter papers to give, as a monohydrate, potassium (1S)-D-lyxit-1-ylsulfonate (0.396 g, 41%), m.p. 392–400 K (with decomposition); $[\alpha]_{\text{D}} 7.1$ (30 min.) (c , 0.75 in 9:1 H₂O:HOAc). ¹H NMR (D₂O, 400 MHz, reference *Me*₃COH at δ_{H} 1.24): δ_{H} 4.93 (d , $J_{1,2} = 4.5$ Hz, H-1 of α -pyranose), 4.86 (d , $J_{1,2} = 1.5$ Hz, H-1 of β -pyranose); signals for the major acyclic sulfonate: δ_{H} 4.70 (d , $J_{1,2} = 1$ Hz, H-1), 4.19 (dd , $J_{2,3} = 9.4$ Hz, H-2), 3.99 (td , $J_{3,4} = 6.5$, $J_{4,5b} = 6.5$, $J_{4,5a} = 1.5$ Hz, H-4), 3.62 (dd , $J_{5a,5b} = -9.4$, H-5a); for the minor acyclic sulfonate: δ_{H} 4.62 (d , $J_{1,2} = 5.5$ Hz, H-1); ratio of major

to minor sulfonate = 10:1. ¹³C NMR (D₂O, 100 MHz, reference *Me*₃COH at δ_{C} 30.29): δ_{C} 94.86 (C1, β -pyranose), 94.70 (C1, α -pyranose); signals for the major acyclic sulfonate: δ_{C} 82.20 (C1), 70.45, 69.88, 69.35 (C2, C3, C4), 63.80 (C5); the minor acyclic sulfonate showed a peak at δ_{C} 84.26 (C1).

Integration of the various signals for H-1 in the ¹H NMR spectrum, five minutes after sample dissolution, indicated the species α -pyranose, β -pyranose, major acyclic sulfonate and minor acyclic sulfonate were present in the % ratios of 35.48: 11.29: 48.39: 4.84. In the more concentrated solution prepared for ¹³C NMR the corresponding ratios were 17.05:5.43: 71.32:6.20.

HRESMS (negative ion mode, measured in H₂O/MeOH, solution) gave a peak at m/z 149.0457 ([C₅H₉O₅]⁻), a significant peak at 213.0073 ([C₅H₁₁O₈S - H₂O]⁻), and the base peak at 299.0979 ([C₁₀H₁₉O₁₀]⁻). The latter corresponds to the ion of the product formed by reaction between the bisulfite adduct and D-lyxose with displacement of potassium bisulfite. No significant peak was observed for ([C₅H₁₁O₈S]⁻) at the calculated m/z of 231.0180.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the hydrogen atoms were located in difference maps and were refined freely.

Acknowledgements

We thank the EPSRC National Mass Spectrometry Facility (NMSF), Swansea, for determination of the low- and high-resolution mass spectra and Dr Sergey Nepogodiev for measurement of the NMR spectra.

References

- Agilent (2014). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, England.
- Cole, E. R., Craig, D. C., Fitzpatrick, L. J., Hibbert, D. B. & Stevens, J. D. (2001). *Carbohydr. Res.* **335**, 1–10.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Gehman, H. & Osman, E. M. (1954). *Adv. Food Res.* **5**, 53–96.
- Haines, A. H. & Hughes, D. L. (2010). *Carbohydr. Res.* **345**, 2705–2708.
- Haines, A. H. & Hughes, D. L. (2012). *Acta Cryst.* **E68**, m377–m378.
- Haines, A. H. & Hughes, D. L. (2013). *Acta Cryst.* **E69**, m7–m8.
- Haines, A. H. & Hughes, D. L. (2014). *Acta Cryst.* **E70**, 406–409.
- Ingles, D. L. (1959). *Aust. J. Chem.* **12**, 97–101.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.

supporting information

Acta Cryst. (2015). E71, 993-996 [doi:10.1107/S2056989015014139]

Crystal structure of potassium (1S)-D-lyxit-1-ylsulfonate monohydrate

Alan H. Haines and David L. Hughes

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP* (Johnson, 1976) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012).

Potassium (1S,2S,3S,4R)-1,2,3,4,5-pentahydroxypentane-1-sulfonate monohydrate

Crystal data

$K^+ \cdot C_5H_{11}O_8S^- \cdot H_2O$

$M_r = 288.31$

Orthorhombic, $P2_12_12$

$a = 23.3536$ (5) Å

$b = 9.0434$ (2) Å

$c = 4.9939$ (1) Å

$V = 1054.69$ (4) Å³

$Z = 4$

$F(000) = 600$

$D_x = 1.816$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10753 reflections

$\theta = 3.5$ – 32.6°

$\mu = 0.74$ mm⁻¹

$T = 140$ K

Square prism, colourless

$0.28 \times 0.26 \times 0.11$ mm

Data collection

Oxford Diffraction Xcalibur 3/Sapphire3 CCD diffractometer

Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: 16.0050 pixels mm⁻¹

Thin slice φ and ω scans

Absorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2014)

$T_{\min} = 0.914$, $T_{\max} = 1.000$

20712 measured reflections

3062 independent reflections

3008 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 3.5^\circ$

$h = -32 \rightarrow 32$

$k = -12 \rightarrow 12$

$l = -7 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.048$

$S = 1.12$

3062 reflections

198 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 0.2102P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.30$ e Å⁻³

$\Delta\rho_{\min} = -0.34$ e Å⁻³

Absolute structure: Flack x determined using
 1229 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: 0.023 (11)

Special details

Experimental. CrysAlisPro, Agilent Technologies, Version 1.171.36.21 Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.5000	1.0000	0.67598 (9)	0.01296 (9)
K2	0.5000	0.5000	0.70830 (10)	0.01438 (9)
C1	0.37190 (6)	0.69370 (16)	0.3668 (3)	0.0102 (3)
C2	0.32071 (6)	0.69562 (16)	0.1730 (3)	0.0099 (2)
C3	0.26543 (6)	0.67837 (15)	0.3346 (3)	0.0104 (3)
C4	0.21277 (6)	0.65562 (16)	0.1567 (3)	0.0112 (3)
C5	0.15984 (6)	0.63560 (19)	0.3308 (3)	0.0150 (3)
O1	0.38531 (5)	0.55224 (13)	0.4618 (2)	0.0142 (2)
O2	0.32388 (5)	0.57866 (13)	-0.0172 (2)	0.0129 (2)
O3	0.26007 (5)	0.81265 (13)	0.4827 (3)	0.0138 (2)
O4	0.20578 (5)	0.77316 (14)	-0.0315 (2)	0.0136 (2)
O5	0.10823 (5)	0.62153 (13)	0.1783 (3)	0.0156 (2)
S1	0.43316 (2)	0.78331 (4)	0.21337 (7)	0.00910 (8)
O11	0.43680 (5)	0.73320 (13)	-0.0636 (2)	0.0145 (2)
O12	0.48337 (4)	0.74113 (13)	0.3723 (2)	0.0132 (2)
O13	0.42133 (5)	0.94196 (12)	0.2349 (3)	0.0153 (2)
O9	0.42697 (5)	0.37107 (14)	1.0868 (3)	0.0188 (2)
H1	0.3619 (8)	0.756 (2)	0.520 (4)	0.008 (4)*
H2	0.3170 (9)	0.786 (2)	0.088 (4)	0.014 (5)*
H3	0.2694 (9)	0.598 (2)	0.456 (5)	0.015 (5)*
H4	0.2190 (9)	0.573 (2)	0.044 (5)	0.017 (5)*
H5A	0.1557 (9)	0.718 (3)	0.447 (5)	0.019 (5)*
H5B	0.1647 (9)	0.553 (3)	0.444 (5)	0.019 (6)*
H1O	0.3898 (10)	0.496 (3)	0.338 (5)	0.029 (6)*
H2O	0.3515 (10)	0.585 (3)	-0.100 (5)	0.021 (6)*
H3O	0.2443 (11)	0.793 (3)	0.633 (5)	0.029 (7)*
H4O	0.2011 (12)	0.848 (3)	0.035 (6)	0.037 (8)*
H5O	0.1126 (10)	0.557 (3)	0.075 (5)	0.023 (6)*
H9A	0.4115 (12)	0.304 (3)	1.008 (7)	0.042 (8)*
H9B	0.4524 (13)	0.326 (3)	1.175 (7)	0.048 (8)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.01062 (18)	0.01409 (18)	0.0142 (2)	-0.00037 (15)	0.000	0.000
K2	0.0152 (2)	0.01494 (19)	0.01297 (19)	0.00403 (16)	0.000	0.000
C1	0.0088 (6)	0.0117 (6)	0.0101 (6)	0.0001 (5)	0.0004 (5)	0.0014 (5)
C2	0.0087 (6)	0.0110 (6)	0.0100 (6)	0.0001 (5)	0.0000 (5)	0.0008 (5)
C3	0.0092 (6)	0.0104 (6)	0.0117 (7)	-0.0003 (5)	0.0008 (5)	0.0005 (5)
C4	0.0090 (6)	0.0116 (6)	0.0129 (7)	-0.0005 (5)	0.0004 (5)	0.0010 (6)
C5	0.0096 (6)	0.0205 (7)	0.0151 (7)	-0.0016 (5)	0.0001 (6)	0.0022 (6)
O1	0.0163 (5)	0.0135 (5)	0.0128 (5)	0.0002 (4)	-0.0024 (4)	0.0041 (4)
O2	0.0099 (5)	0.0172 (5)	0.0118 (5)	-0.0010 (4)	0.0020 (4)	-0.0032 (4)
O3	0.0140 (5)	0.0139 (5)	0.0133 (5)	-0.0014 (4)	0.0028 (4)	-0.0036 (4)
O4	0.0147 (5)	0.0146 (5)	0.0116 (5)	0.0015 (4)	-0.0002 (4)	0.0012 (4)
O5	0.0083 (5)	0.0201 (5)	0.0184 (6)	-0.0014 (4)	-0.0008 (4)	-0.0038 (5)
S1	0.00803 (14)	0.01074 (14)	0.00852 (15)	-0.00035 (11)	0.00023 (12)	0.00024 (12)
O11	0.0150 (5)	0.0200 (5)	0.0084 (5)	-0.0009 (5)	0.0011 (4)	-0.0014 (4)
O12	0.0091 (4)	0.0182 (5)	0.0124 (5)	0.0006 (4)	-0.0011 (4)	0.0013 (4)
O13	0.0160 (5)	0.0107 (4)	0.0191 (6)	-0.0006 (4)	-0.0015 (4)	0.0003 (4)
O9	0.0141 (5)	0.0159 (6)	0.0263 (6)	0.0020 (5)	-0.0060 (5)	-0.0015 (5)

Geometric parameters (\AA , $^\circ$)

K1—O12 ⁱ	2.8161 (12)	C2—O2	1.4233 (18)
K1—O12	2.8162 (12)	C2—C3	1.530 (2)
K1—O5 ⁱⁱ	2.8505 (11)	C2—H2	0.93 (2)
K1—O5 ⁱⁱⁱ	2.8505 (11)	C3—O3	1.4274 (18)
K1—O13	2.9160 (12)	C3—C4	1.531 (2)
K1—O13 ⁱ	2.9160 (12)	C3—H3	0.95 (2)
K1—O11 ^{iv}	3.1131 (12)	C4—O4	1.4281 (18)
K1—O11 ^v	3.1131 (12)	C4—C5	1.522 (2)
K1—O13 ^{iv}	3.3824 (13)	C4—H4	0.95 (2)
K1—O13 ^v	3.3824 (13)	C5—O5	1.4313 (18)
K1—S1 ⁱ	3.4078 (5)	C5—H5A	0.95 (2)
K1—S1	3.4079 (5)	C5—H5B	0.94 (2)
K2—O12	2.7787 (12)	O1—H1O	0.80 (3)
K2—O12 ^{vi}	2.7787 (12)	O2—H2O	0.77 (3)
K2—O9	2.8002 (14)	O3—H3O	0.85 (3)
K2—O9 ^{vi}	2.8003 (14)	O4—H4O	0.76 (3)
K2—O11 ^v	2.8149 (12)	O5—K1 ^x	2.8505 (11)
K2—O11 ^{vii}	2.8149 (12)	O5—H5O	0.78 (3)
K2—O1	2.9854 (12)	S1—O11	1.4579 (11)
K2—O1 ^{vi}	2.9855 (12)	S1—O13	1.4650 (11)
K2—K1 ^{viii}	4.5246 (1)	S1—O12	1.4665 (11)
K2—K2 ^v	4.9939 (1)	S1—K1 ^{ix}	3.6713 (5)
K2—K2 ^{ix}	4.9939 (1)	O11—K2 ^{ix}	2.8149 (12)
K2—H9B	3.02 (3)	O11—K1 ^{ix}	3.1131 (12)
C1—O1	1.3998 (18)	O13—K1 ^{ix}	3.3824 (13)

C1—C2	1.538 (2)	O9—H9A	0.81 (3)
C1—S1	1.8141 (15)	O9—H9B	0.84 (3)
C1—H1	0.98 (2)		
O12 ⁱ —K1—O12	114.84 (5)	O9 ^{vi} —K2—K1 ^{viii}	116.12 (3)
O12 ⁱ —K1—O5 ⁱⁱ	109.61 (3)	O11 ^v —K2—K1 ^{viii}	139.74 (2)
O12—K1—O5 ⁱⁱ	86.51 (3)	O11 ^{vii} —K2—K1 ^{viii}	42.75 (2)
O12 ⁱ —K1—O5 ⁱⁱⁱ	86.51 (3)	O1—K2—K1 ^{viii}	98.25 (2)
O12—K1—O5 ⁱⁱⁱ	109.61 (3)	O1 ^{vi} —K2—K1 ^{viii}	80.05 (2)
O5 ⁱⁱ —K1—O5 ⁱⁱⁱ	150.43 (6)	K1—K2—K1 ^{viii}	175.911 (17)
O12 ⁱ —K1—O13	80.20 (3)	O12—K2—K2 ^v	127.14 (3)
O12—K1—O13	49.96 (3)	O12 ^{vi} —K2—K2 ^v	127.14 (3)
O5 ⁱⁱ —K1—O13	133.00 (4)	O9—K2—K2 ^v	47.55 (3)
O5 ⁱⁱⁱ —K1—O13	72.75 (3)	O9 ^{vi} —K2—K2 ^v	47.55 (3)
O12 ⁱ —K1—O13 ⁱ	49.96 (3)	O11 ^v —K2—K2 ^v	66.13 (2)
O12—K1—O13 ⁱ	80.20 (3)	O11 ^{vii} —K2—K2 ^v	66.13 (2)
O5 ⁱⁱ —K1—O13 ⁱ	72.76 (3)	O1—K2—K2 ^v	114.35 (3)
O5 ⁱⁱⁱ —K1—O13 ⁱ	133.00 (4)	O1 ^{vi} —K2—K2 ^v	114.35 (3)
O13—K1—O13 ⁱ	81.87 (5)	K1—K2—K2 ^v	92.044 (9)
O12 ⁱ —K1—O11 ^{iv}	61.01 (3)	K1 ^{viii} —K2—K2 ^v	92.044 (9)
O12—K1—O11 ^{iv}	159.17 (3)	O12—K2—K2 ^{ix}	52.86 (3)
O5 ⁱⁱ —K1—O11 ^{iv}	76.81 (3)	O12 ^{vi} —K2—K2 ^{ix}	52.86 (3)
O5 ⁱⁱⁱ —K1—O11 ^{iv}	90.86 (3)	O9—K2—K2 ^{ix}	132.45 (3)
O13—K1—O11 ^{iv}	138.92 (3)	O9 ^{vi} —K2—K2 ^{ix}	132.45 (3)
O13 ⁱ —K1—O11 ^{iv}	82.96 (3)	O11 ^v —K2—K2 ^{ix}	113.87 (2)
O12 ⁱ —K1—O11 ^v	159.16 (3)	O11 ^{vii} —K2—K2 ^{ix}	113.87 (2)
O12—K1—O11 ^v	61.01 (3)	O1—K2—K2 ^{ix}	65.65 (3)
O5 ⁱⁱ —K1—O11 ^v	90.86 (3)	O1 ^{vi} —K2—K2 ^{ix}	65.65 (3)
O5 ⁱⁱⁱ —K1—O11 ^v	76.81 (3)	K1—K2—K2 ^{ix}	87.956 (9)
O13—K1—O11 ^v	82.96 (3)	K1 ^{viii} —K2—K2 ^{ix}	87.956 (9)
O13 ⁱ —K1—O11 ^v	138.92 (3)	K2 ^v —K2—K2 ^{ix}	180.0
O11 ^{iv} —K1—O11 ^v	130.61 (4)	O12—K2—H9B	145.3 (6)
O12 ⁱ —K1—O13 ^{iv}	103.91 (3)	O12 ^{vi} —K2—H9B	96.3 (6)
O12—K1—O13 ^{iv}	130.41 (3)	O9—K2—H9B	16.1 (6)
O5 ⁱⁱ —K1—O13 ^{iv}	50.78 (3)	O9 ^{vi} —K2—H9B	85.4 (6)
O5 ⁱⁱⁱ —K1—O13 ^{iv}	102.19 (3)	O11 ^v —K2—H9B	83.3 (6)
O13—K1—O13 ^{iv}	173.46 (3)	O11 ^{vii} —K2—H9B	59.4 (6)
O13 ⁱ —K1—O13 ^{iv}	104.67 (3)	O1—K2—H9B	94.0 (6)
O11 ^{iv} —K1—O13 ^{iv}	43.74 (3)	O1 ^{vi} —K2—H9B	124.5 (6)
O11 ^v —K1—O13 ^{iv}	91.89 (3)	K1—K2—H9B	123.1 (6)
O12 ⁱ —K1—O13 ^v	130.41 (3)	K1 ^{viii} —K2—H9B	60.6 (6)
O12—K1—O13 ^v	103.91 (3)	K2 ^v —K2—H9B	39.5 (6)
O5 ⁱⁱ —K1—O13 ^v	102.19 (3)	K2 ^{ix} —K2—H9B	140.5 (6)
O5 ⁱⁱⁱ —K1—O13 ^v	50.78 (3)	O1—C1—C2	113.41 (12)
O13—K1—O13 ^v	104.67 (3)	O1—C1—S1	112.02 (10)
O13 ⁱ —K1—O13 ^v	173.46 (3)	C2—C1—S1	110.00 (10)
O11 ^{iv} —K1—O13 ^v	91.89 (3)	O1—C1—H1	108.2 (12)
O11 ^v —K1—O13 ^v	43.74 (3)	C2—C1—H1	107.6 (11)

O13 ^{iv} —K1—O13 ^v	68.79 (4)	S1—C1—H1	105.2 (11)
O12 ⁱ —K1—S1 ⁱ	25.01 (2)	O2—C2—C3	108.66 (11)
O12—K1—S1 ⁱ	100.14 (3)	O2—C2—C1	111.77 (11)
O5 ⁱⁱ —K1—S1 ⁱ	89.35 (3)	C3—C2—C1	108.82 (12)
O5 ⁱⁱⁱ —K1—S1 ⁱ	110.94 (3)	O2—C2—H2	110.9 (13)
O13—K1—S1 ⁱ	83.10 (3)	C3—C2—H2	104.6 (13)
O13 ⁱ —K1—S1 ⁱ	25.29 (2)	C1—C2—H2	111.7 (13)
O11 ^{iv} —K1—S1 ⁱ	67.69 (2)	O3—C3—C2	105.10 (11)
O11 ^v —K1—S1 ⁱ	161.09 (2)	O3—C3—C4	110.15 (12)
O13 ^{iv} —K1—S1 ⁱ	102.79 (2)	C2—C3—C4	112.67 (12)
O13 ^v —K1—S1 ⁱ	153.82 (2)	O3—C3—H3	109.2 (14)
O12 ⁱ —K1—S1	100.14 (3)	C2—C3—H3	109.4 (14)
O12—K1—S1	25.01 (2)	C4—C3—H3	110.2 (13)
O5 ⁱⁱ —K1—S1	110.94 (3)	O4—C4—C5	111.81 (12)
O5 ⁱⁱⁱ —K1—S1	89.34 (3)	O4—C4—C3	111.94 (12)
O13—K1—S1	25.29 (2)	C5—C4—C3	109.69 (12)
O13 ⁱ —K1—S1	83.11 (3)	O4—C4—H4	102.4 (14)
O11 ^{iv} —K1—S1	161.09 (2)	C5—C4—H4	111.7 (14)
O11 ^v —K1—S1	67.69 (2)	C3—C4—H4	109.1 (13)
O13 ^{iv} —K1—S1	153.82 (2)	O5—C5—C4	113.00 (13)
O13 ^v —K1—S1	102.79 (2)	O5—C5—H5A	108.0 (13)
S1 ⁱ —K1—S1	94.639 (16)	C4—C5—H5A	109.8 (13)
O12—K2—O12 ^{vi}	105.71 (5)	O5—C5—H5B	110.5 (13)
O12—K2—O9	130.48 (3)	C4—C5—H5B	109.7 (13)
O12 ^{vi} —K2—O9	99.55 (3)	H5A—C5—H5B	105.5 (19)
O12—K2—O9 ^{vi}	99.55 (3)	C1—O1—K2	119.01 (9)
O12 ^{vi} —K2—O9 ^{vi}	130.48 (3)	C1—O1—H1O	110.1 (19)
O9—K2—O9 ^{vi}	95.09 (6)	K2—O1—H1O	95.8 (18)
O12—K2—O11 ^v	65.36 (3)	C2—O2—H2O	110.5 (18)
O12 ^{vi} —K2—O11 ^v	154.90 (3)	C3—O3—H3O	108.4 (18)
O9—K2—O11 ^v	73.70 (4)	C4—O4—H4O	113 (2)
O9 ^{vi} —K2—O11 ^v	74.59 (4)	C5—O5—K1 ^x	130.19 (10)
O12—K2—O11 ^{vii}	154.90 (3)	C5—O5—H5O	107.9 (17)
O12 ^{vi} —K2—O11 ^{vii}	65.36 (3)	K1 ^x —O5—H5O	89.8 (17)
O9—K2—O11 ^{vii}	74.59 (4)	O11—S1—O13	112.64 (7)
O9 ^{vi} —K2—O11 ^{vii}	73.70 (4)	O11—S1—O12	112.71 (7)
O11 ^v —K2—O11 ^{vii}	132.26 (5)	O13—S1—O12	111.46 (7)
O12—K2—O1	60.09 (3)	O11—S1—C1	107.93 (7)
O12 ^{vi} —K2—O1	90.03 (3)	O13—S1—C1	104.94 (7)
O9—K2—O1	78.33 (4)	O12—S1—C1	106.60 (7)
O9 ^{vi} —K2—O1	139.37 (4)	O11—S1—K1	142.67 (5)
O11 ^v —K2—O1	65.03 (3)	O13—S1—K1	58.23 (5)
O11 ^{vii} —K2—O1	139.10 (3)	O12—S1—K1	54.30 (5)
O12—K2—O1 ^{vi}	90.03 (3)	C1—S1—K1	109.38 (5)
O12 ^{vi} —K2—O1 ^{vi}	60.10 (3)	O11—S1—K1 ^{ix}	56.47 (5)
O9—K2—O1 ^{vi}	139.37 (4)	O13—S1—K1 ^{ix}	67.11 (5)
O9 ^{vi} —K2—O1 ^{vi}	78.33 (4)	O12—S1—K1 ^{ix}	101.22 (5)
O11 ^v —K2—O1 ^{vi}	139.10 (3)	C1—S1—K1 ^{ix}	151.95 (5)

O11 ^{vii} —K2—O1 ^{vi}	65.03 (3)	K1—S1—K1 ^{ix}	89.650 (8)
O1—K2—O1 ^{vi}	131.29 (5)	S1—O11—K2 ^{ix}	130.34 (7)
O12—K2—K1	36.31 (2)	S1—O11—K1 ^{ix}	100.55 (6)
O12 ^{vi} —K2—K1	139.71 (3)	K2 ^{ix} —O11—K1 ^{ix}	99.38 (3)
O9—K2—K1	116.12 (3)	S1—O12—K2	130.00 (6)
O9 ^{vi} —K2—K1	66.92 (3)	S1—O12—K1	100.69 (6)
O11 ^v —K2—K1	42.75 (2)	K2—O12—K1	107.94 (4)
O11 ^{vii} —K2—K1	139.74 (2)	S1—O13—K1	96.48 (6)
O1—K2—K1	80.05 (2)	S1—O13—K1 ^{ix}	89.37 (5)
O1 ^{vi} —K2—K1	98.25 (2)	K1—O13—K1 ^{ix}	104.67 (3)
O12—K2—K1 ^{viii}	139.71 (3)	K2—O9—H9A	105 (2)
O12 ^{vi} —K2—K1 ^{viii}	36.31 (2)	K2—O9—H9B	97 (2)
O9—K2—K1 ^{viii}	66.92 (3)	H9A—O9—H9B	102 (3)
O1—C1—C2—O2	-44.09 (16)	O13—S1—O11—K2 ^{ix}	150.63 (7)
S1—C1—C2—O2	82.24 (13)	O12—S1—O11—K2 ^{ix}	23.46 (10)
O1—C1—C2—C3	75.92 (15)	C1—S1—O11—K2 ^{ix}	-93.99 (9)
S1—C1—C2—C3	-157.75 (10)	K1—S1—O11—K2 ^{ix}	83.82 (10)
O2—C2—C3—O3	-169.41 (11)	K1 ^{ix} —S1—O11—K2 ^{ix}	112.07 (8)
C1—C2—C3—O3	68.67 (14)	O13—S1—O11—K1 ^{ix}	38.57 (7)
O2—C2—C3—C4	-49.45 (15)	O12—S1—O11—K1 ^{ix}	-88.61 (6)
C1—C2—C3—C4	-171.36 (11)	C1—S1—O11—K1 ^{ix}	153.94 (5)
O3—C3—C4—O4	60.33 (15)	K1—S1—O11—K1 ^{ix}	-28.25 (9)
C2—C3—C4—O4	-56.67 (16)	O11—S1—O12—K2	-95.90 (9)
O3—C3—C4—C5	-64.38 (15)	O13—S1—O12—K2	136.30 (8)
C2—C3—C4—C5	178.61 (12)	C1—S1—O12—K2	22.33 (10)
O4—C4—C5—O5	52.08 (17)	K1—S1—O12—K2	124.57 (9)
C3—C4—C5—O5	176.87 (12)	K1 ^{ix} —S1—O12—K2	-154.07 (6)
C2—C1—O1—K2	162.60 (8)	O11—S1—O12—K1	139.53 (6)
S1—C1—O1—K2	37.34 (13)	O13—S1—O12—K1	11.73 (7)
C4—C5—O5—K1 ^x	159.72 (9)	C1—S1—O12—K1	-102.24 (6)
O1—C1—S1—O11	84.07 (12)	K1 ^{ix} —S1—O12—K1	81.36 (3)
C2—C1—S1—O11	-43.04 (11)	O11—S1—O13—K1	-139.03 (6)
O1—C1—S1—O13	-155.59 (11)	O12—S1—O13—K1	-11.20 (7)
C2—C1—S1—O13	77.30 (11)	C1—S1—O13—K1	103.80 (6)
O1—C1—S1—O12	-37.26 (12)	K1 ^{ix} —S1—O13—K1	-104.69 (4)
C2—C1—S1—O12	-164.36 (10)	O11—S1—O13—K1 ^{ix}	-34.34 (6)
O1—C1—S1—K1	-94.52 (10)	O12—S1—O13—K1 ^{ix}	93.50 (6)
C2—C1—S1—K1	138.37 (8)	C1—S1—O13—K1 ^{ix}	-151.50 (5)
O1—C1—S1—K1 ^{ix}	135.22 (9)	K1—S1—O13—K1 ^{ix}	104.69 (4)
C2—C1—S1—K1 ^{ix}	8.11 (18)		

Symmetry codes: (i) $-x+1, -y+2, z$; (ii) $x+1/2, -y+3/2, -z+1$; (iii) $-x+1/2, y+1/2, -z+1$; (iv) $-x+1, -y+2, z+1$; (v) $x, y, z+1$; (vi) $-x+1, -y+1, z$; (vii) $-x+1, -y+1, z+1$; (viii) $x, y-1, z$; (ix) $x, y, z-1$; (x) $-x+1/2, y-1/2, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots O9 ^{ix}	0.80 (3)	1.90 (3)	2.6716 (19)	160 (2)

O2—H2O...O1 ^{ix}	0.77 (3)	2.35 (3)	2.9810 (17)	141 (2)
O2—H2O...O11	0.77 (3)	2.41 (2)	2.9935 (16)	134 (2)
O3—H3O...O4 ^v	0.85 (3)	1.91 (3)	2.7609 (17)	173 (3)
O4—H4O...O2 ^{xi}	0.76 (3)	2.17 (3)	2.8586 (17)	151 (3)
O5—H5O...O13 ^{xii}	0.78 (3)	2.03 (3)	2.7152 (17)	146 (2)
O9—H9A...O5 ^x	0.81 (3)	1.95 (3)	2.7426 (18)	167 (3)
O9—H9B...O12 ^{vii}	0.84 (3)	1.90 (3)	2.7289 (17)	170 (3)

Symmetry codes: (v) $x, y, z+1$; (vii) $-x+1, -y+1, z+1$; (ix) $x, y, z-1$; (x) $-x+1/2, y-1/2, -z+1$; (xi) $-x+1/2, y+1/2, -z$; (xii) $-x+1/2, y-1/2, -z$.